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(54) Process for the selective preparation of alkenecarboxylic acid derivatives.

(57) A process for the selective carbonylation of conjugated dienes in the presence of a hydroxyl group containing compound such as water, alcohol, phenol or carboxylic acid, in the liquid phase, characterized in that this carbonylation is carried out in the presence of a specific substantially organic nitrogen-containing base-free catalyst system, that can be formed by the combination of

(a) a palladium compound and
(b) at least one multidentate organic phosphorus ligand.

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PROCESS FOR THE SELECTIVE PREPARATION OF ALKENECARBOXYLIC ACID DERIVATIVES

The present invention relates to a process for the preparation of alkenecarboxylic acid derivatives by carbonylation of conjugated dienes and, in particular, to the preparation of 3-pentenoic acid and higher homologues from 1,3-butadiene and higher conjugated dienes.

Processes for the carbonylation of olefinically unsaturated hydrocarbons are inter alia known from British Patent Specification No. 1,110,405 and from US Patent Specifications Nos. 4,172,087 and 4,414,409.

In British Patent Specification No. 1,110,405 a process is described for the preparation of esters by the reaction of a diene with carbon monoxide and an alcohol or phenol in the presence of a catalyst containing platinum, palladium and/or nickel and/or

(a) bromide and/or iodide ions or

(b) a ligand that is able to form a co-ordination linkage with the metal component of the catalyst and that contains nitrogen, phosphorus, arsenic or sulphur, preference being given to trivalent phosphorus-containing ligands, and particular preference to a primary, secondary or tertiary phosphine or an alkyl, aryl or cycloalkyl phosphite.

Although the conversion of butadiene is mentioned as one of the embodiments, preference is clearly given on page 2, lines 97-103 to dienes as starting compounds, wherein the double bonds are separated by 2, 3 or 4 single bonds, while, moreover, the reaction is preferably performed in an acidified reaction medium, for example, in the presence of toluenesulphonic acid.

From the yields of pent-3-enoate as described in the relevant examples, it will be clear to a person skilled in the art that the aforesaid British Patent Specification certainly does not provide any indications for the very selective preparation of pent-3-enoate and higher homologues from 1,3-butadiene and higher conjugated dienes.

From US Patent Specification No. 4,172,087 a process is known for the simultaneous preparation of two groups of unsaturated carboxylic acids and esters thereof from conjugated aliphatic diene starting materials containing from 4 to 8 carbon atoms, wherein:

(a) every two moles of the conjugated aliphatic diene concerned are mixed with a three-component mixture consisting of

i. at least a catalytic quantity of a palladium catalyst consisting of either one or more palladium halides in combination with one or more monodentate tertiary phosphorus-containing donor ligands, or one or more palladium halide-free salts in combination with one or more multidentate, tertiary phosphorus-containing donor ligands,

ii. at least one molar equivalent of a hydroxyl group containing co-reactant selected from the group consisting of water or an aliphatic alcohol containing 1 to 12 carbon atoms, and

iii. an (N-heterocyclic) amine base,

(b) the reaction mixture is pressurized with sufficient carbon monoxide to satisfy the stoichiometry of the carbonylation reaction,

(c) the pressurized reaction mixture is heated until substantial formation of the desired aliphatic carboxylic acid derivatives has been achieved, and

(d) the unsaturated carboxylic acid derivatives concerned that occur therein are isolated.

Although the conversion of 1,3-butadiene and conjugated aliphatic diene are mentioned, the presence of an N-heterocyclic base, such as pyridine, alkylated pyridines, quinoline, lutidine, picolene, isoquinoline, alkylated quinolines and isoquinolines, acridine and N-methyl-2-pyrrolidone or N,N-dimethylaniline, N,N-diethylaniline, N,N-diethyltoluidine, N,N-dibutyl-toluidine and N,N-dimethylformamide is considered to be an essential precondition.

In particular, from the yields of pent-3-enoate mentioned in the described examples, it will be clear to a person skilled in the art that the process according to the aforesaid US Patent Specification No. 4,172,087 certainly gives no indications for a very selective preparation of pent-3-enoate and higher homologues from 1,3-butadiene and higher conjugated dienes.

From US Patent Specification No. 4,414,409 a carbonylation process is known for the preparation of acids and esters by conversion of an olefinically unsaturated compound, carbon monoxide and a hydroxyl compound at about 50 ° to about 150 °C, in the presence of a catalyst consisting of an organic phosphine ligand palladium complex and a perfluorosulphonic acid.

A clear preference is, moreover, indicated in column 2, lines 26-29 and in column 9, line 27 for the conversion of non-conjugated hydrocarbons.

It will be clear that the processes described hereinbefore are either unsuitable for the conversion of conjugated unsaturated compounds or, in particular, do not seem to be suited to a very selective

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preparation of 3-pentenoic acid or derivatives and higher homologues, and that those skilled in the art, searching for improved selective preparation methods for 3-pentenoic acid and derivatives thereof, which are becoming increasingly important starting materials for organic syntheses (for example for the preparation of adipic acid and derivatives thereof), have been diverted away from the methods described hereinbefore.

More in general, a number of known processes have the disadvantage that relatively high concentrations of the relevant catalyst system are used and also aggressive reaction components, for example acids such as hydrohalogenic acids or salts thereof and other rigorous reaction conditions, which necessitate cost-increasing measures in connection with safety and the apparatus life (corrosion).

Object of the present invention, therefore, is to provide an improved very selective carbonylation of 1,3-butadiene and higher homologues to very valuable products, such as 3-pentenoic acid or derivatives thereof.

An improved process has now, surprisingly, been found for the selective conversion of conjugated dienes such as 1,3-butadiene, 1,4-hexadiene and 2,4-heptadiene in the liquid phase with a generally increased conversion rate, in the presence of a characteristic catalyst system and without the necessity of (N-heterocyclic) amines and/or halides, thus allowing cheaper types of steel for the reactor installations.

The present invention therefore relates to a process for the selective carbonylation of conjugated dienes in the presence of a hydroxyl group containing compound such as water, an alcohol, a phenol or a carboxylic acid, in the liquid phase and in the presence of a specific substantially organic nitrogen-containing base-free catalyst system, that can be formed by combination of

(a) a palladium compound and
(b) at least one multidentate organic phosphorus ligand.

In particular, the aforesaid process is carried out in the presence of a catalyst system that can be formed by a combination of

(a) a palladium compound and
(b) at least one bidentate phosphine derivative with the general formula

$$R_1R_2 > P - R - P < R_3R_4 \qquad (I)$$

where R_1, R_2, R_3 and R_4 represent hydrocarbyl groups optionally substituted with one or more substituents and R represents a divalent organic bridging group with at least 2 carbon atoms forming the bridge.

Preferably, the groups R_1 and R_3 represent an optionally substituted aryl group, preferably phenyl or naphthyl, the groups R_2 and R_4 represent an optionally substituted alkyl group of 1-20 carbon atoms and preferably 2-6 carbon atoms, a cycloalkyl group or an aryl group, and the group R an alkylene group of 2-6 carbon atoms, a phenylene or cycloalkylene group.

The aforesaid hydrocarbyl groups can themselves be substituted with alkyl or alkoxy of 1-4 carbon atoms, halogen and preferably fluorine or chlorine.

According to a preferred embodiment, it is possible, depending on the other catalyst components chosen, to add a catalytic quantity of a protonic acid with a pKa value > 3 to increase the yield of, for example, pentenoates, in the case of conversion of butadiene at approximately constant high selectivity. The selectivity of, for example, 3-pentenoic acid or derivatives thereof, expressed as percentage, is defined as

$$\frac{a}{b} \times 100$$

where "a" is the quantity of 1,3-butadiene converted into 3-pentenoic acid or derivatives thereof, and "b" the total quantity of converted 1,3-butadiene.

It will be clear that the very high selectivity that has been found for the conversion of, for example, 1,3-butadiene into 3-pentenoic acid and derivatives thereof is obtained at the cost of 3,8-nonadienic acid or derivatives thereof, 4-vinyl-1-cyclohexene and 1,3,7-octatriene, which in the known earlier processes, are also formed simultaneously.

Examples of particularly suitable phosphorus ligands are:
1,2-di(diphenylphosphino) ethane,
1,3-di(diphenylphosphino) propane,
1,4-di(diphenylphosphino) butane,
1,5-di(diphenylphosphino) pentane,
1,6-di(diphenylphosphino) hexane,
1,2-tetrafluorocyclobutene diyl bis diphenyl phosphine;

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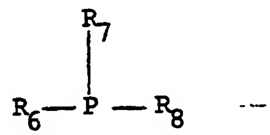
1,2-phenylene bis diphenyl phosphine,
1,2-ethane diyl bis(ditrifluoromethyl) phosphine,
1,3-propane diyl bis(ditrifluoromethyl) phosphine,
1,3-propane diyl bis(trifluoromethyl phenyl) phosphine,
1,2-hexafluorocyclopentene diyl bis diphenyl phosphine,
1,2-tetrafluorocyclobutene diyl bis diphenyl phosphine,
1,2-octafluorocyclohexene diyl bis diphenyl phosphine,
1,4-diphenyl-1,4-diphosphacyclohexane or mixtures thereof.

Very good results are obtained with 1,4-di(diphenylphosphino) butane, 1,3-di(diphenylphosphino) propane or 1,5-di(diphenylphosphino) pentane or mixtures thereof. Moreover, it has been found that good relative conversion results can be obtained if, in addition to the multidentate and preferably bidentate phosphine ligands that are in any case present in the said catalyst system, one or more monodentate phosphine ligands are also present. A particularly preferred group of these last-mentioned compounds includes the group represented by the general formula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where R_6 represents an optionally substituted aryl group and preferably a phenyl or naphthyl group and R_7 and R_8 each represent an optionally substituted alkyl, optionally substituted cycloalkyl or optionally substituted aryl group, or wherein R_7 and R_8 together represent an optionally substituted alkylene or phosphacyclo-alkylene group. Mixtures of these phosphines can also be employed. Preferably, each alkyl group herein contains up to 20 carbon atoms, each cycloalkyl group up to 7 carbon atoms in the ring and each aryl group up to 18 carbon atoms in the ring. An aryl group can represent an anthryl, naphthyl or phenyl group. Phosphines according to formula II, in which R_6 and R_7 each represent an optionally substituted phenyl group, form a preferred group. Within this group phosphines in which R_8 also represents an optionally substituted phenyl group, form a particularly preferred group.

The protonic acids with pKa value >3, which may be added to the catalyst system, are preferably benzoic acid or benzoic acids substituted with one or more electron-repelling groups such as 2,4,6-trimethyl benzoic acid, para hydroxybenzoic acid and meta hydroxybenzoic acid.

Both homogeneous and heterogeneous palladium catalyst components can be used for the selective conversion according to the present invention. However, homogeneous catalyst systems are preferred. Suitable homogeneous catalyst components are palladium salts of, for example, nitric acid, sulphuric acid or alkane carboxylic acids containing not more than 12 carbon atoms. Of these, palladium(II) acetate is preferred. However, palladium complexes, such as palladium acetylacetonate, o-toluylphosphinepalladium acetate or bistriphenylphosphinepalladium sulphate can also be used. Palladium linked to an ion exchanger, for example an ion exchanger containing sulphonic acid groups, is an example of a suitable heterogeneous catalyst component. The quantity of palladium is not critical. If a divalent palladium compound is used, preference is given to the use of quantities in the range of from 10^{5} to 10^{1} gram atoms of palladium per mol of conjugated diene and preferably butadiene.

It has been found that for the best results the molar ratio of the organic phosphorus compound relative to palladium should not be greater than 10 mol phosphine per gram atom of palladium. Very high selectivities and very high conversion rates are obtained if the molar ratio of the phosphine to palladium is between 2 and 5 mol per gram atom of palladium (e.g. 100% conversion of butadiene in 5 hours at 150 °C). It has been found that the proportion of the protonic acid with pKa value >3 - when added - should preferably be in the range of from 6 to 10 equivalents of acid per gram atom of palladium.

A separate solvent is not essential for the process according to the present invention, and often an excess of one of the reactants or products will form a suitable liquid phase. In some cases, however, it may be desirable to use a separate solvent. Any inert solvent can, in principle, be used for this purpose. This can, for example, be chosen from sulphoxides and sulphones, for example dimethyl sulphoxide, diisopropyl sulphone or tetrahydro thiophene 1,1-dioxide (also referred to as sulfolane), 2-methyl-4-butyl sulfolane, 3-methyl sulfolane; aromatic hydrocarbons such as benzene, toluene, xylenes; esters such as methyl acetate and butyrolactone; ketones such as acetone or methyl-isobutyl ketone; and ethers such as anisole, 2,5,8-trioxanone (also referred to as diglyme), diphenyl ether and diisopropyl ether or mixtures thereof. Prefer-

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ably, diphenyl ether is used.

The process according to the present invention enables relatively mild reaction conditions to be used. Temperatures of from 50° to 150 °C and more in particular from 20° to 200 °C have been found to be very suitable.

The initial pressure of the carbon monoxide can vary over a wide range, but will in general be lower than that of hitherto known processes. Pressures of from 25 to 65 bar are preferred.

In the process according to the present invention, the carbon monoxide can be used in its pure form or diluted with an inert gas such as nitrogen, noble gases or carbon dioxide. In general, the presence of more than 5% hydrogen is undesirable, since this can cause hydrogenation of the conjugated diene under the reaction conditions.

The molar ratio of alcohol, phenol, water or carboxylic acid relative to conjugated diene, in particular butadiene, can vary between wide limits and generally lies in the range of 0.1:1 to 10:1.

According to a preferred embodiment of the process according to the present invention, an alcohol can be used as hydroxyl containing reactant. The alcohol can be aliphatic, cycloaliphatic or aromatic and can, if necessary, carry one or more inert substituents. A suitable alcohol can comprise up to 20 carbon atoms. One or more hydroxyl groups can be present, in which case different products may be formed. For example, a polyvalent alcohol, in particular lower sugars such as glucose, fructose, mannose, galactose, sucrose, aldoxose, aldopentose, altrose, talose, gulose, idose, ribose, arabinose, xylose, lyxose, erythrose or threose, can be reacted with a suitable quantity of butadiene to form a monoester or a polyvalent ester. The choice of the alcohol will therefore only depend on the desired product. Alkanols such as methanol, ethanol, propanol or 2,2-dihydroxymethyl-1-butanol and alcohols containing ether bridges, such as triethylene glycol, all give valuable products.

According to another embodiment of the process according to the present invention, a great variety of carboxylic acids can be used as reactant. For example, the carboxylic acids can be aliphatic, cycloaliphatic or aromatic and may possibly carry inert substituents. Suitable carboxylic acids comprise a maximum of 25 carbon atoms. The carboxylic acids used as reactant are preferably alkane carboxylic acids or alkene carboxylic acids. Typical examples of suitable carboxylic acids are formic acid, acetic acid, propionic acid, n-butyric acid, isobutyric acid, pivalic acid, n-valeric acid, n-caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, phthalic acid and terephthalic acid. Examples of alkene carboxylic acids are acrylic acid, propiolic acid, methacrylic acid, crotonic acid, isocrotonic acid, oleic acid, maleic acid, fumaric acid, citraconic acid and mesaconic acid.

The process according to the present invention can in principle also be carried out with polyvalent carboxylic acids, whereby, depending on the chosen reaction conditions, including the molar ratio of the reactants used, a variety of products can be obtained as required. If an alkane carboxylic acid is converted according to the process of the invention with 1,3-butadiene, a symmetrical or a mixed anhydride can be formed.

Preferably, weak acids are used for the process according to the invention, with pKa value >3 measured in an aqueous medium at 18 °C.

Even more preference is given to the use of acids that cannot be esterified, or only with difficulty, in connection with losses during the process.

The process according to the present invention has been found to be particularly suitable for continuous processes, i.e. repeated use of the relevant catalyst system, which offers great advantages for use on industrial scale.

The present invention also relates to a substantially organic nitrogen-containing base-free catalyst system for the selective carbonylation of conjugated dienes in the presence of a hydroxyl group containing compound such as an alcohol, a phenol, a carboxylic acid or water, comprising

(a) a palladium compound and

(b) at least one bidentate phosphine derivative with the general formula

$$R_1R_2 > P - R - P < R_3R_4 \qquad (I)$$

where R_1, R_2, R_3 and R_4 represent hydrocarbyl groups optionally substituted with one or more substituents and R represents a divalent organic bridging group with at least 2 carbon atoms forming the bridge,

(c) a monodentate phosphine derivative.

In a catalyst system according to the present invention preferably a protonic acid with a pKa value >3 is included.

Preferably, the groups R_1 and R_3 represent an optionally substituted aryl group, preferably phenyl or naphthyl, the groups R_2 and R_4 represent an optionally substituted alkyl group of 1-20 carbon atoms and

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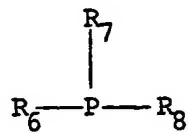
preferably 2-6 carbon atoms, a cycloalkyl group or an aryl group, and the group R an alkylene group of 2-6 carbon atoms, a phenylene or cycloalkylene group.

Examples of particularly suitable phosphorus ligands in catalyst systems according to the present invention are those as described hereinbefore.

Suitable monodentate phosphine ligands present in a catalyst system according to the present invention can be selected from the group represented by the formula



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where R_6 represents an optionally substituted aryl group and preferably a phenyl or naphthyl group and R_7 and R_8 each represent an optionally substituted alkyl, optionally substituted cycloalkyl or optionally substituted aryl group, or wherein R_7 and R_8 together represent an optionally substituted alkylene or phosphacyclo-alkylene group or mixtures thereof.

Phosphines according to formula II in which R_6, R_7 and R_8 each represent an optionally substituted phenyl group, form a preferred group.

The protonic acids with pKa value >3, which may be added to a catalyst system according to the present invention, preferably consist of benzoic acid or benzoic acids substituted with one or more electron-repelling groups such as 2,4,6-trimethyl benzoic acid, para hydroxybenzoic acid and meta hydroxybenzoic acid.

Preferred catalyst systems according to the invention comprise palladium(II) acetate as homogeneous catalyst component. Moreover, very high selectivities and very high conversion rates can be obtained if the molar ratio of the phosphine to palladium in these catalysts is between 2 and 5 mol per gram atom of palladium.

In a catalyst system according to the present invention the proportion of the possibly added protonic acid with pKa value >3 should preferably be 6-10 equivalents of acid per gram atom of palladium.

Preferred catalyst systems comprise an additional solvent. This additional solvent can, for example, be chosen from the sulphoxides and sulphones as described hereinbefore.

The invention will now be illustrated by the following Examples.

Example 1

A 300 ml magnetically stirred Hastelloy® (the word Hastelloy is a Registered Trade Mark) autoclave was successively filled with 15 ml ethanol, 40 ml diphenyl ether, 1 mmol palladium acetate and 5 mmol 1,4-di(diphenylphosphino) butane. The autoclave was evaluated, whereupon 8 ml of butadiene and carbon monoxide were added to an initial carbon monoxide pressure of 60 bar. The autoclave was heated to 155 °C. After a reaction time of 5 hours, the contents of the autoclave were analyzed by means of gas-liquid chromatography. The selectivity of the butadiene to pentenoate conversion was found to be 95%, while the pentenoate yield was 30%, calculated on the starting quantity of butadiene.

Example 2

In a virtually analogous manner as described in Example 1, an experiment was carried out with a catalyst system comprising palladium acetate (1mmol) and 1,3-di(diphenylphosphino) propane (1.5 mmol). The selectivity of the butadiene to pentenoate conversion was found to be 92%, while the pentenoate yield, calculated on the starting quantity of butadiene, was 50%.

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Example 3

In a virtually analogous manner as described in Example 1, an experiment was carried out with a catalyst system comprising 1 mmol palladium acetate,2 mmol 1,4-di(diphenylphosphino) butane and 5 mmol triphenyl phosphine. The selectivity found for the butadiene to pentenoate conversion was 93%, while the pentenoate yield, calculated on the starting quantity of butadiene, was found to be 50%.

Example 4

In a virtually analogous manner as described in Example 1, an experiment was carried out with a catalyst system comprising 1 mmol palladium acetate, 4 mmol 1,4-di(diphenylphosphino) butane and 7.5 mmol 2,4,6-trimethyl benzoic acid. The reaction temperature was 150 °C and the reaction time was 2.5 hours. The selectivity of the butadiene to pentenoate conversion was found to be 96%, while the pentenoate yield, calculated on the starting quantity of butadiene, was 90%.

Example 5

In a virtually analogous manner as described in Example 1, an experiment was carried out with a catalyst system comprising 1 mmol palladium acetate, 4 mmol 1,4-di(diphenylphosphino) butane, 4 mmol triphenyl phosphine and 7.5 mmol 2,4,6-trimethyl benzoic acid. The reaction temperature was 150 °C and the reaction time was 2.5 hours. The selectivity of the butadiene to pentenoate conversion was found to be 91%, while the pentenoate yield, calculated on the starting quantity of butadiene, was found to be 88%.

Example 6

In a virtually analogous manner as described in Example 1, an experiment was carried out with a catalyst system comprising 1 mmol palladium acetate, 4 mmol 1,4-di(diphenylphosphino) butane and 7.5 mmol 2,4,6-trimethyl benzoic acid. The initial pressure of the carbon monoxide was 30 bar. The reaction temperature was 150 °C and the reaction time was 2.5 hours. The selectivity of the butadiene to pentenoate conversion was 90%, while the pentenoate yield, calculated on the starting quantity of butadiene, was found to be 89%.

Example 7

In a virtually analogous manner as described in Example 1, a comparative experiment was carried out with a catalyst system comprising 1 mmol palladium acetate, 10 mmol triphenyl phosphine and 7.5 mmol 2,4,6-trimethyl benzoic acid. The reaction temperature was 150 °C and the reaction time was 2.5 hours. The selectivity found for the butadiene to pentenoate conversion was 75% (15% of the butadiene was found to have been converted into nonadienoates) and the pentenoate yield, calculated on the starting quantity of butadiene, was 55%.

Example 8

In a virtually analogous manner as described in Example 1, an experiment was carried out with a catalyst system comprising 1 mmol palladium acetate and 1.5 mmol 1,2-di(diphenylphosphino) ethane. The selectivity found for the butadiene to pentenoate conversion was 88%, while the pentenoate yield, calculated on the starting quantity of butadiene, was 40%.

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Example 9

In a virtually analogous manner as described in Example 1, an experiment was carried out with a catalyst system comprising 1 mmol palladium acetate and 4 mmol 1,2,4-di(diphenylphosphino) butane and 7.5 mmol 2,4,6-trimethyl benzoic acid. During the reaction time of 10 hours, additional ethanol and butadiene were added at dosing rates of 25 mmol ethanol/hour and 25 mmol butadiene/hour. The selectivity found for the butadiene to pentenoate conversion was 90%, while the pentenoate yield, calculated on the starting quantity of butadiene, was 81%.

Claims

1. A process for the selective carbonylation of conjugated dienes in the presence of a hydroxyl group containing compound such as water, alcohol, phenol or carboxylic acid, in the liquid phase, characterized in that this carbonylation is carried out in the presence of a specific substantially organic nitrogen-containing base-free catalyst system, that can be formed by the combination of

(a) a palladium compound and

(b) at least one multidentate organic phosphorus ligand.

2. A process according to claim 1, characterized in that this is carried out in the presence of a catalyst system that can be formed by the combination of

(a) a palladium compound and

(b) at least one bidentate phosphine derivative with the general formula

$$R_1R_2 > P - R - P < R_3R_4 \quad (I)$$

where R_1, R_2, R_3 and R_4 represent hydrocarbyl groups optionally substituted with one or more substituents and R represents a divalent organic bridging group with at least 2 carbon atoms forming the bridge.

3. A process according to claim 2, characterized in that the groups R_1 and R_3 represent an optionally substituted aryl group, preferably phenyl or naphthyl, the groups R_2 and R_4 an optionally substituted alkyl group of 1-20 carbon atoms and preferably 2-6 carbon atoms, a cycloalkyl group or an aryl group, and the group R an alkylene group of 2-6 carbon atoms, a phenylene or cycloalkylene group.

4. A process according to claim 2 or 3, characterized in that the hydrocarbyl groups can be substituted with alkyl or alkoxy of 1-4 carbon atoms and halogen.

5. A process according to any one of claims 1-4, characterized in that a catalytic quantity of a protonic acid with a pKa value >3 is added.

6. A process according to claim 5, characterized in that benzoic acid or a benzoic acid substituted with one or more electron-repelling groups such as 2,4,6-trimethyl benzoic acid, para hydroxybenzoic acid or meta hydroxybenzoic acid is used as protonic acid.

7. A process according to any one of claims 1-6, characterized in that the following are used as phosphorus ligands:

1,2-di(diphenylphosphino) ethane,
1,3-di(diphenylphosphino) propane,
1,4-di(diphenylphosphino) butane,
1,5-di(diphenylphosphino) pentane,
1,6-di(diphenylphosphino) hexane,
1,2-tetrafluorocyclobutene diyl bis diphenyl phosphine,
1,2-phenylene bis diphenyl phosphine,
1,2-ethane diyl bis(ditrifluoromethyl) phosphine,
1,3-propane diyl bis(ditrifluoromethyl) phosphine,
1,3-propane diyl bis(trifluoromethyl phenyl) phosphine,
1,2-hexafluorocyclopentene diyl bis diphenyl phosphine,
1,2-tetrafluorocyclobutene diyl bis diphenyl phosphine,
1,2-octafluorocyclohexene diyl bis diphenyl phosphine,
1,4-diphenyl-1,4-diphosphacyclohexane or mixtures thereof.

8. A process according to any one of claims 1-7, characterized in that 1,4-di(diphenylphosphino) butane, 1,3-di(diphenylphosphino) propane or 1,5-di(diphenylphosphino) pentane or mixtures thereof are used.

9. A process according to any one of claims 1-8, characterized in that in addition to the bidentate phosphorus ligands present, one or more monodentate ligands are also present.

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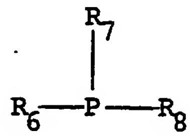
10. A process according to claim 9, characterized in that phosphorus ligands according to the following general formula are used:



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where R_6 represents an optionally substituted aryl group and preferably a phenyl or naphthyl group and R_7 and R_8 each represent an optionally substituted alkyl, optionally substituted cycloalkyl or optionally substituted aryl group, or wherein R_7 and R_8 together represent an optionally substituted alkylene or phosphacyclo-alkylene group, or mixtures thereof.

11. A process according to claim 10, characterized in that phosphine ligands are used in which R_6, R_7 and R_8 represent an optionally substituted phenyl group.

12. A process according to any one of claims 1-11, characterized in that palladium(II) acetate is used.

13. A process according to any one of claims 1-12, characterized in that a quantity of 10^{5} to 10^{1} gram atoms palladium per mol conjugated diene - preferably butadiene - is used.

14. A process according to any one of claims 1-13, characterized in that the molar ratio of phosphine to palladium is between 2 and 5 mol per gram atom palladium.

15. A process according to any one of claims 1-14, characterized in that 6-10 equivalents of the protonic acid with a pKa value >3 per gram atom palladium is used.

16. A process according to any one of claims 1-15, characterized in that an additional solvent is used chosen from sulphoxides and sulphones, for example dimethyl sulphoxide, diisopropyl sulphone, tetrahydrothiophene 1,1-dioxide (sulfolane), 2-methyl-4-butyl sulfolane, or 3-methyl sulfolane; aromatic hydrocarbons such as benzene, toluene, xylenes; esters such as methyl acetate and butyrolactone; ketones such as acetone or methyl isobutyl ketone; and ethers such as anisole, 2,5,8-trioxanone (diglyme), diphenyl ether and diisopropyl ether or mixtures thereof is used.

17. A process according to claim 16, characterized in that diphenyl ether is used.

18. A process according to any one of claims 1-17, characterized in that the molar quantity of alcohol, phenol, water or carboxylic acid per mol diene lies between 0.1:1 and 10:1.

19. A process according to any one of claims 1-18, characterized in that 1,3-butadiene is converted.

20. A substantially organic nitrogen-containing base-free catalyst system for the selective carbonylation of conjugated dienes in the presence of a hydroxyl group containing compound such as alcohol, phenol, carboxylic acid or water, characterized in that this comprises:

(a) a palladium compound and

(b) at least one bidentate phosphine derivative with the general formula

$$R_1R_2 > P - R - P < R_3R_4 \qquad (I)$$

where R_1, R_2, R_3 and R_4 represent hydrocarbyl groups optionally substituted with one or more substituents and R represents a divalent organic bridging group with at least 2 carbon atoms forming the bridge,

(c) a monodentate phosphine derivative.

21. A catalyst system according to claim 20, characterized in that a protonic acid with a pKa value >3 is included.

22. A catalytic system according to claim 21, characterized in that herein benzoic acid or benzoic acids substituted with one or more electron-repelling groups such as 2,4,6-trimethyl benzoic acid, para hydroxybenzoic acid and meta hydroxybenzoic acid are included.

23. A catalytic system according to any one of claims 20-23, characterized in that the bidentate phosphine ligand consists of 1,4-di(diphenylphosphino) butane, 1,3-di(diphenylphosphino) propane or 1,5-di-(diphenylphosphino) pentane.

24. A catalyst system according to any one of claims 20-23, characterized in that an additional solvent is included.

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(54) **Process for the selective preparation of alkenecarboxylic acid derivatives.**

(57) A process for the selective carbonylation of conjugated dienes in the presence of a hydroxyl group containing compound such as water, alcohol, phenol or carboxylic acid, in the liquid phase, characterized in that this carbonylation is carried out in the presence of a specific substantially organic nitrogen-containing base-free catalyst system, that can be formed by the combination of

(a) a palladium compound and

(b) at least one multidentate organic phosphorus ligand.

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EUROPEAN SEARCH REPORT

Application Number

EP 87 20 2334

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP-A-0 190 473 (SHELL) * Column 2, line 1 - column 4, line 67; column 6, lines 31-55 *	1	C 07 C 67/38 C 07 C 69/533
A	EP-A-0 198 521 (SHELL) * Page 2, line 27 - page 5, line 17; pages 13-14, claims 1,3,4,7 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 67/00 C 07 C 69/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-03-1988	KINZINGER J.M.

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